Synopsis

In this thesis, the thermal decomposition investigation of haloethanols namely 2-chloroethanol and 2-bromoethanol are reported both experimental and theoretical. Computational calculation of enthalpy of formation haloethanols using isodesmic and atomization reactions has also been reported. Finally, the chemistry of JP-10 ignition has also been investigated using shock tube.

Chapter 1 gives a brief introduction to the experimental shock tube technique. Brief surveys of literature pertinent to haloethanols and JP-10 have also been discussed. The importance of thermal rate coefficient and detection techniques in shock tube chemistry is presented. Details of the theoretical methods used in the determination of thermal rate coefficients have been described at the end of the chapter.

In Chapter 2, I have discussed experimental methods used in carrying out this work. The details of the experimental shock tube set-up employed in this work have been elaborated in this chapter. Kinetic simulations performed to understand the mechanism of chemical transformation of haloethanols at high temperature have also been presented.

In chapter 3, thermal decomposition results obtained for 2-chloroethanol have been described. The kinetic data have been obtained in the temperature range of 930-1100 K behind the reflected shock wave in a shock tube. Analyses of pre and post shock mixture using FT-IR and gas chromatographic techniques are presented. Chemical kinetic simulation performed to simulate the product distribution is presented. The reduced kinetic model has also been presented which was obtained using the sensitivity analysis and was validated by comparison to the shock

tube measurements. The details of the β-substitution effect have been shown. The kinetic parameters of the unimolecular elimination of HCl and H_2O have been presented both experimentally and theoretically. Theoretical results were obtained by transition state theory using quantum chemistry calculations HF, MP2 (FULL) and B3LYP/6-311++G** level of theory. The details of intrinsic reaction coordinate calculation and potential energy surface calculations have also been described. These experimental and theoretical results suggest that the rate of HCl elimination is faster than that of H_2O and HOCl elimination reaction.

In chapter 4, I have reported thermal decomposition results obtained for 2-bromoethanol. The kinetic data have been obtained in the temperature range of 910-1102 K behind the reflected shock wave in a shock tube. Analyses of pre and post shock mixture using FT-IR and gas chromatographic techniques are discussed. Chemical kinetic simulation performed to simulate the product distribution is presented. The details of the β-substitution effect are explained. Both experimental and theoretical kinetic parameters of the unimolecular elimination of HBr and H_2O have been presented. Theoretical results were obtained by transition state theory using quantum chemistry calculations at the HF, MP2 (FULL) and B3LYP/6-311++G** level of theory. The intrinsic reaction coordinate calculation and potential energy surface have been investigated in details. From this experimental and theoretical studies, it has been concluded that the rate of HBr elimination much faster than that of H_2O. However, the experiments show that the rate of HOBr elimination is faster than that of the H_2O.

In chapter 5, I have reported the computational calculation of enthalpy of formation of haloethanols. The enthalpy of formation of haloethanols of the general formula XC_2H_4OH were calculated by the HF, MP2, B3LYP, G2, G3, G2MP2, G3B3, G3MP2B3, CBS-Q, CBS-QB3 and CCSD/cc-pVDZ level of theories applying isodesmic and atomization reactions. Results

obtained using the Benson's group and bond additivity methods have also been described at 298.15 K and at 1 atm in the gaseous state.

In chapter 6, ignition delay measurement on neat jet propellent-10 (JP-10) and JP-10 + Triethyl amine (TEA) mixture have been reported. The JP-10 (Exo-tetrahydrodicyclopentadiene, $C_{10}H_{16}$) ignition delay times were measured behind a single pulse reflected shock wave in a shock tube. Experiments were performed over high temperature, high pressure, and three equivalence ratio and for different composition. It has been shown that the TEA can reduce the ignition delay of JP-10. A higher level quantum chemistry calculation has also been presented that were performed to obtain the bond dissociation energies of C-H bonds in JP-10.

Chapter7 is the concluding chapter where the main work done in this thesis is summarized and future direction is presented.